CLAIMS

1. A hydraulic cement based on calcium phosphate for surgical use comprising
A) a first component comprising powder particles of calcium phosphate; and
B) a second component comprising water
characterized in that
C) said calcium phosphate comprises anhydrous, amorphous calcium phosphate (ACP); and
D) said ACP is obtained by milling a calcium phosphate synthesized above 500°C.

2. A hydraulic cement according to claim 1, characterized in that said ACP is obtained by milling of one or more substances chosen from the group of
a) α-tricalcium phosphate [(α-TCP; $Ca_3(PO_4)_2$] ;
b) β-tricalcium phosphate [(β-TCP; $Ca_3(PO_4)_2$] ;
c) oxyapatite [(OXA); $Ca_{10}(PO_4)_6O$];
d) tetracalciumphosphate [TetCP; $Ca_4(PO_4)_2O$]
in the presence of not more than 20 weight percent of a non-aqueous auxiliary milling liquid compared to 100 weight percent of calcium phosphate.

3. Cement according to claim 2, characterized that the auxiliary milling solvent is an alcohol, preferably ethanol, or isopropanol.

4. Cement according to one of the claims 1 to 3, characterized in that additionally to said ACP it contains one or several other calcium phosphates from the following list: monocalcium phosphate (MCP; $Ca(H_2PO_4)_2$); monocalcium phosphate monohydrate (MCPM; $Ca(H_2PO_4)_2.H_2O$), dicalcium phosphate (DCP; $CaHPO_4$), dicalcium phosphate dihydrate (DCPD; $CaHPO_4.2H_2O$); Octocalcium phosphate (OCP; $Ca_8H_2(PO_4)6.5H_2O$); calcium deficient hydroxyapatite (CDHA; $Ca_9(HPO_4)(PO_4)_5OH$), hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$), beta-tricalcium phosphate (b-TCP; Ca3(PO4)2), oxyapatite (OXA; $Ca_{10}(PO_4)_6O$), tetracalcium phosphate (TTCP; $Ca_4(PO_4)_2O$), and a-tricalcium phosphate.

5. Cement according to one of the claims 1 to 4, characterized in that the amorphous calcium phosphate (ACP) is present in an amount of at least 50 weight percent of the total first component.

6. Cement according to claim 5, characterized in that the amorphous calcium phosphate (ACP) is present in an amount of at least 80 weight percent, preferably of at least 90 weight percent of the total first component.

7. Cement according to one of the claims 1 to 6, characterized in that said first component comprises an amount of calcium sulfate dihydrate (CSD).

8. Cement according to claim 7, characterized in that it does not contain more calcium sulfate hemihydrate (CSH) than 10 % of the total amount of said calcium sulfate dihydrate (CSD).

9. Cement according to one of the claims 1 to 8, characterized in that said first component comprises an amount of calcium sulfate hemihydrate (CSH).

10. Cement according to claim 9, characterized in that the amount of calcium sulfate hemihydrate (CSH) is lower than 5% of said calcium sulfate dihydrate (CSD).

11. Cement according to claim 10, characterized in that essentially no calcium sulfate hemihydrate (CSH) is detectable in the cement.

12. Cement according to one of the claims 1 to 11, characterized in that the powder particles of said first component have an average diameter inferior to 20 μm and preferably inferior to 10 μm.

13. Cement according to one of the claims 1 to 12, characterized in that at least one of the two cement components comprises a setting regulator.

14. Cement according to one of the claims 1 to 13, characterized in that at least one of the cement components comprises a setting accelerator.

15. Cement according to claim 14, characterized in that the first component comprises a setting accelerator.

16. Cement according to claim 14 or 15, characterized in that the setting accelerator is an apatite powder.

17. Cement according to claim 14 or 15, characterized in that the setting accelerator is a calcium-deficient hydroxyapatite or hydroxyapatite powder.

18. Cement according to claim 14 or 15, characterized in that the setting accelerator is a water-soluble calcium salt, preferably calcium chloride.

19. Cement according to one of the claims 1 to 18, characterized in that the second component comprises a setting accelerator.

20. Cement according to one of the claims 1 to 19, characterized in that the setting accelerator is a dissolved calcium salt, preferably calcium chloride.

21. Cement according to one of the claims 1 to 20, characterized in that the setting regulator is a setting retarder.

22. Cement according to one of the claims 1 to claim 21, characterized in that the first or second component comprises a setting retarder.

23. Cement according to claim 21 or 22, characterized in that the setting retarder is taken from the group of citrate, pyrophosphate, carbonate or magnesium ions.

24. Cement according to one of the claims 1 to 23, characterized in that the setting time of the cement paste at 37°C is comprised between 2 and 15 minutes.

25. Cement according to claim 24, characterized in that the setting time of the cement paste at 37°C is comprised between 5 and 12 minutes.

26. Cement according to one of the claims 1 to 25, characterized in that the Ca/P molar ratio of the cement paste obtained by mixing said three components is larger than 1,5.

27. Cement according to claim 26, characterized in that the Ca/P molar ratio of the cement is equal to 1,667.

28. Cement according to claim 26, characterized in that the Ca/P molar ratio of the cement is larger than 1,667.

29. Cement according to claim 26, characterized in that the Ca/P molar ratio of the cement is equal or larger than 2,0.

30. Cement according to one of the claims 1 to 29, characterized in that at least one of the components contains a radiological contrasting agent.

31. Cement according to claim 30, characterized in that the radiological contrasting agent is a solid compound.

32. Cement according to claim 31, characterized in that said solid radiological contrasting agent is present in particle form whereby said particles have a diameter larger than 10 micrometer, more preferably larger than 20 micrometer.

33. Cement according to claim 31 or 32 characterized in that the radiological contrasting agent is a metal powder, preferably of tantalum, tungsten or titanium.

34. Cement according to claim 31 or 32 characterized in that the radiological contrasting agent is a ceramic powder, preferably barium sulfate or titanium dioxide.

35. Cement according to claim 30, characterized in that the radiological contrasting agent is a liquid compound, preferably an iodine compound.

36. Cement according to claim 35, characterized in that the radiological contrasting agent is an organic iodine compound, preferably iopamidol ($C_{17}H_{22}I_3N_3O_8$), iohexol ($C_{19}H_{26}I_3N_3O_9$), or iotrolan ($C_{37}H_{48}I_6N_6O_{18}$).

37. Cement according to one of the claims 1 to 36, characterized in that one of said three components, preferably the third component, comprises an additive to control the cement rheology.

38. Cement according claim 37, characterized in that the third component comprises an additive to control the cement rheology.

39. Cement according to claim 37 or 38, characterized in that the additive used to control the cement rheology is taken from the group of polysaccharide derivatives, preferably hyaluronic acid or salt, chondroitin sulfate, dermantan sulfate, heparan sulfate, heparin, dextran, alginate, keratan sulfate, hydroxypropylmethyl cellulose, chitosan, xanthan gum, guar gum, or carrageenan.

40. Cement according to claim 37 or 38, characterized in that the additive used to control the cement rheology is hyaluronic acid and/or one of its salts.

41. Cement according to one of the claims 37 to 40, characterized in that the concentration of the additive used to control the cement rheology is larger than 1 weight %, preferably superior to 2 weight %, of the third component.

42. Cement according to one of the claims 1 to 41, characterized in that the volume VL of the third component is in the range of $0,5\ VT \leq VL \leq 10,0\ VT$ where VT is the total powder volume of the first and second component.

43. Cement according to claim 42, characterized in that the volume VL of the third component is in the range of $1,0\ VT \leq VL \leq 2,5\ VT$ where VT is the total powder volume of the first and second component.

44. Cement according to one of the claims 1 to 43, characterized in that the first or second component of the cement may further comprise granules whose diameter

are at least two times, preferably at least 10 times larger than the average diameter of said powder particles of said first component.

45. Cement according to claim 44, characterized in that the granules have an average diameter in the range of 100 μm to 500 μm.

46. Cement according to claim 44 or 45, characterized in that the granules are made of calcium phosphate, CSH, CSD, polymer, sodium chloride, bioglass or a sugar, preferably glucose, fructose, and mannose.

47. Cement according to one of the claims 1 to 46, characterized in that one or more of said three components comprises pharmaceutically or physiologically active substances, preferably antibiotics, anti-inflammatory drugs, drugs against osteoporosis, anti-cancer drugs, peptides, proton-pump inhibitors and proteins such as growth factors.

48. Cement according to one of the claims 1 to 47, characterized in that the one of said three components, preferably the third component, comprises a tensio-active agent, preferably taken from the group of: docusate sodium ($C_{20}H_{37}NaO_7S$), sodium lauryl sulfate ($C_{12}H_{25}NaO_4S$), stearic acid ($C_{17}H_{35}COOH$), alkyldimethyl(phenylmethyl)-ammonium chloride [CAS registry number 8001-54-5], benzethonium chloride ($C_{27}H_{42}ClNO_2$), cetrimide ($C_{17}H_{38}BrN$), glycerin monooleate ($C_{21}H_{40}O_4$), polysorbate 20 ($C_{58}H_{114}O_{26}$), polysorbate 21 ($C_{26}H_{50}O_{10}$), polysorbate 40 ($C_{62}H_{122}O_{26}$), polysorbate 60 ($C_{64}H_{126}O_{26}$), polysorbate 61 ($C_{32}H_{62}O_{10}$), polysorbate 65 ($C_{100}H_{194}O_{28}$), polysorbate 80 ($C_{64}H_{124}O_{26}$), polysorbate 81 ($C_{34}H_{64}O_{11}$), polysorbate 85 ($C_{100}H_{188}O_{28}$), polysorbate 120 ($C_{64}H_{126}O_{26}$), polyvinyl alcohol ($(C_2H_4O)_n$), sorbitan di-isostearate ($C_{42}H_{80}O_7$), sorbitan dioleate ($C_{42}H_{76}O_7$), sorbitan monoisostearate ($C_{24}H_{46}O_6$), sorbitan monolaurate ($C_{18}H_{34}O_6$), sorbitan monooleate ($C_{24}H_{44}O_6$), sorbitan monopalmitate ($C_{22}H_{42}O_6$), sorbitan monostearate ($C_{24}H_{46}O_6$), sorbitan sesqui-isostearate ($C_{33}H_{63}O_{6.5}$), sorbitan sesquioleate ($C_{33}H_{63}O_{6.5}$), sorbitan sesquistearate ($C_{33}H_{63}O_{6.5}$), sorbitan tri-isostearate ($C_{33}H_{63}O_{6.5}$), sorbitan trioleate ($C_{33}H_{63}O_{6.5}$), sorbitan tristearate ($C_{33}H_{63}O_{6.5}$), glyceryl monooleate ($C_{21}H_{40}O_4$), isopropyl myristate ($C_{17}H_{34}O_2$), isopropyl palmitate ($C_{19}H_{38}O_2$), lanolin [CAS registry number 8006-54-0], lanolin alcohols [CAS registry number 8027-33-6], hydrous

lanolin [CAS registry number 8020-84-6], lecithin [CAS registry number 8002-43-5], medium chain triglycerides (no registry number), monoethanolamine (C_2H_7NO), oleic acid ($C_{17}H_{33}COOH$), polyethylene glycol monocetyl ether [CAS registry number 9004-95-9], polyethylene glycol monostearyl ether [CAS registry number 9005-00-9], polyethylene glycol monolauryl ether [CAS registry number 9002-92-0], polyethylene glycol monooleyl ether [CAS registry number 9004-98-2], polyethoxylated castor oil [CAS registry number 61791-12-6], polyoxyl 40 stearate ($C_{98}H_{196}O_{42}$), polyoxyl 50 stearate ($C_{118}H_{236}O_{52}$), triethanolamine ($C_6H_{15}NO_3$), anionic emulsifying wax [CAS registry number 8014-38-8], nonionic emulsifying wax [CAS registry number 977069-99-0], and sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$).

49. Cement according to one of the claims 1 to 48, characterized in that the specific surface area (SSA) of the powder particles of said first component is in the range of 0,05 to 10,00 m^2/g.

50. Cement according to claim 49, characterized in that the specific surface area (SSA) of the first component is in the range of 1.5 to 3.5 m^2/g"

51. Cement according to one of the claims 1 to 50, characterized in that the cement viscosity of the cement is larger than 1Pa s at a shear rate of 400 s^{-1}, one minute after the start of cement mixing.

52. Cement according to claim 51, characterized in that the cement viscosity of the cement is larger than 10Pa s at a shear rate of 400 s^{-1}, one minute after the start of cement mixing, preferably larger than 100 Pa s.

53. Cement according to claim 52, characterized in that component "a)" additionally comprises water-soluble phosphate salts and component "b)" comprises a polymer, preferably sodium hyaluronate

54. Cement according to one of the claims 1 to 53, characterized in that the setting time of the mixture of said two components is between 2 to 15 minutes, preferably between 5 and 12 minutes.

55. Use of the cement according to one of the claims 1 to 54, characterized in that the mixture of said two components is injected into an animal or human bone defect and set in vivo.

56. Method for producing a matrix of apatite as temporary bone replacement material, characterized in that said two components according to one of the claims 1 to 54 are mixed together and allowed to harden.

57. Temporary bone replacement material obtained by the method according to claim 56, characterized in that it comprises an apatite.

58. Temporary bone replacement material according to claim 57, characterized in that it comprises CSD embedded in said apatite matrix.

59. Granules or blocks obtained by hardening the cement according to one of the claims 1 to 54 for in vivo implants.